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# New lithium-ion polymer battery concept for increased capacity

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## Abstract

Free-standing films of graphite anode and  $\text{LiCoO}_2$  cathode materials were produced using 1 wt.% ultra high molecular weight polyethylene (UHMWPE) as a polymeric binder. The technique of vacuum deposition was used in order to provide the anode and cathode materials with 1  $\mu\text{m}$  thick layers of aluminium and copper, respectively, as current collectors. Porous separators were produced by drawing a UHMWPE film filled with inorganic particles. The anode, separator, and cathode materials were then laminated under heat and pressure to produce a single flat cell. The cells were soaked in a liquid electrolyte and sealed in aluminium laminated plastic bags. Batteries produced in this way were cycled at high rates and after 300 cycles only a slight decrease in capacity was observed. Thanks to the thin current collectors and the small amount of polymeric binder the amount of non-active material in the battery was minimised. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Films; Battery; Electrodes; Cell; Lithium; Polymer; UHMWPE

## 1. Introduction

The recent developments in the field of portable electronic equipment have been the main driving force behind the search for batteries with a high energy density and form flexibility. Lithium is a very attractive material for high energy density batteries because of its low weight and high potential. The research into lithium batteries which began in the 1950s has led to the current rechargeable lithium-ion batteries [1] which are rapidly replacing bulkier nickel–cadmium and nickel–metal hydride cells in portable electronic devices. In commercially available rechargeable lithium batteries, materials such as  $\text{LiMnO}_2$  or  $\text{LiCoO}_2$  are used in the cathode while carbon or graphite is used as the anode material. Such a combination of materials results in a battery with a high average open circuit potential ( $V_{\text{oc}}$ ) and a high energy density.

One of the trends in the field is to produce thin batteries with form flexibility. Many attempts have been made to produce such batteries with composite anode and cathodes made up of inorganic particles held together by polymers. In this polymer battery concept, anode and cathode materials are brought onto metallic grid current collectors. They are subsequently laminated using the same polymer as separa-

tor. In this way, a laminated polymer battery can be produced. Various materials ranging from solid polymer electrolytes [2] to the gel electrolytes [3] described above have been suggested for the production of such batteries. The concept suggested by Bellcore [4] is now being commercialised. In this concept, a copolymer of vinylidene fluoride and hexafluoropropylene (PVDF-HFP) is used. The polymer is dissolved in a solvent and appropriate particles are added to the solution to obtain composite electrodes and the separator. After lamination, the solvent is extracted to obtain a porous structure. The laminate is then activated by soaking it in a liquid electrolyte. The battery is subsequently vacuum sealed in aluminium laminated plastic bags.

Here a new method for obtaining free-standing electrodes provided with a thin layer of current collectors is described. The electrodes and the separator are then laminated in a solvent-extraction-free process to produce battery stacks.

## 2. Experimental

The UHMWPE, which was purchased from Aldrich, had a weight average molecular weight of  $M_w > 1 \times 10^6$ . The anode material was produced by dispersing 10 g of mesocarbon microbeads (MCMB) and 0.1 g of ultra high molecular weight polyethylene UHMWPE in 10 g decaline. For the cathode, a dispersion of 10 g  $\text{LiCoO}_2$ , 0.5 g of acetylene-

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black and 0.1 g of UHMWPE in 10 g of decaline was used. The dispersions were heated to 180°C to dissolve the polymer. Solutions were then cast and the solvent was allowed to evaporate. Dry films were rolled to the desired thickness to obtain free-standing films. Current collectors were evaporated directly onto the films under high vacuum. The deposited layer thickness was monitored using a gauge. The materials were mechanically tested using an Instron tester. Porous separators were produced by making films of UHMWPE containing 90%  $\text{LiLa}_{0.35}\text{Ti}_{0.55}\text{O}_3$ . The films were drawn to about three times their original length. In all the experiments, battery grade 1 mol  $\text{LiPF}_6$  in EC:DEC (1:1) (Merck) was used as the liquid electrolyte. The conductivity of the electrolyte in various separators was determined using well-known complex impedance plots obtained using an

HP4194A impedance analyser. The batteries were tested using a Keithley current source and voltmeters.

### 3. Results and discussion

Before describing the electro-chemical behaviour of the electrodes, it is interesting to consider some of their other properties. The anode and cathode materials were produced using the procedure described above. For the purpose of mechanically testing the anode and cathode, materials were produced containing various amounts of UHMWPE in the dry state. The mechanical properties of the materials can be seen in Fig. 1(a) and (b), where the stress is plotted as a function of strain for anode and cathode materials containing

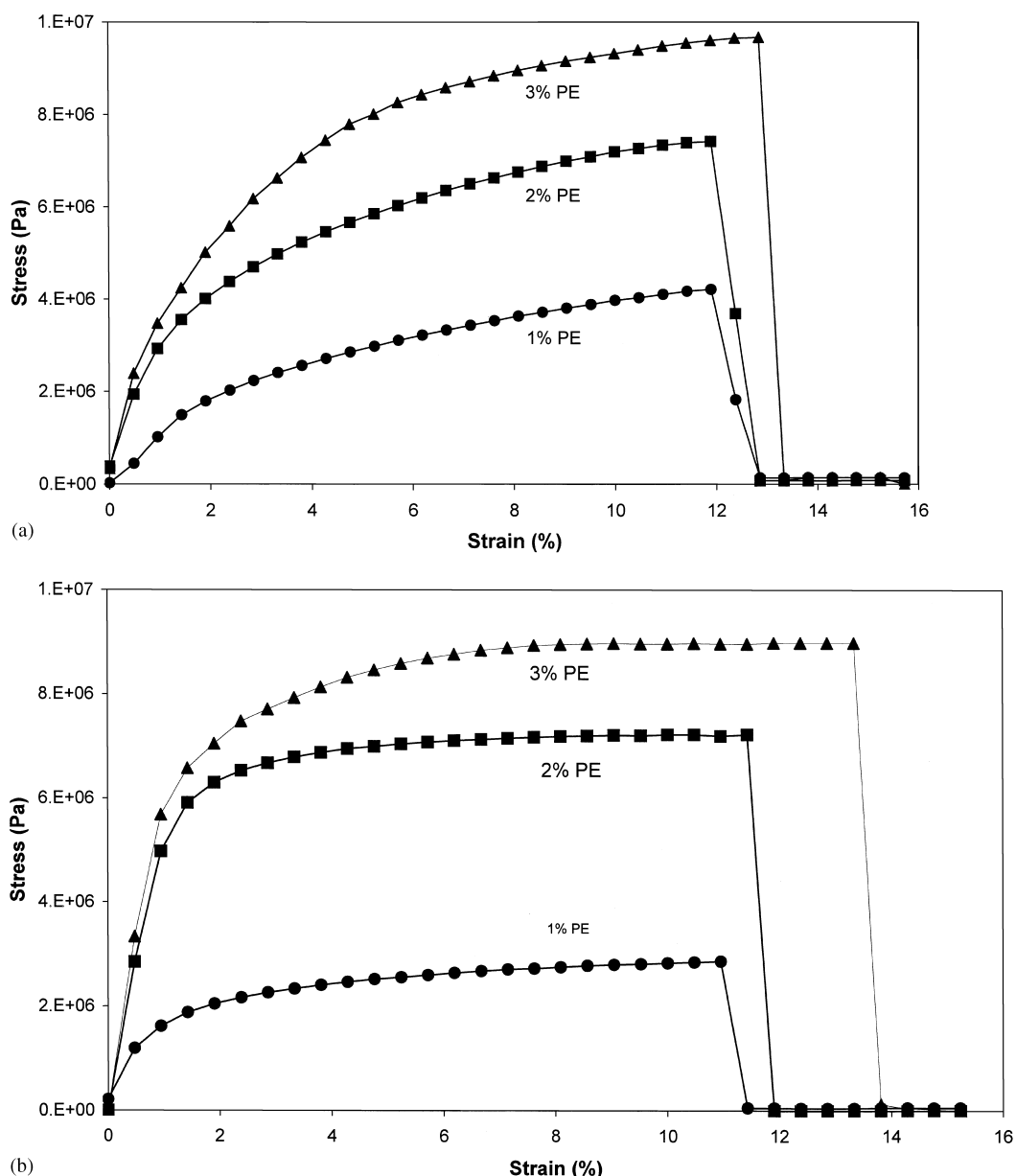


Fig. 1. Stress as a function of strain for (a) anode and (b) cathode materials containing various amounts of polymer. (●) 1%; (■) 2%; (▲) 3 wt.%.

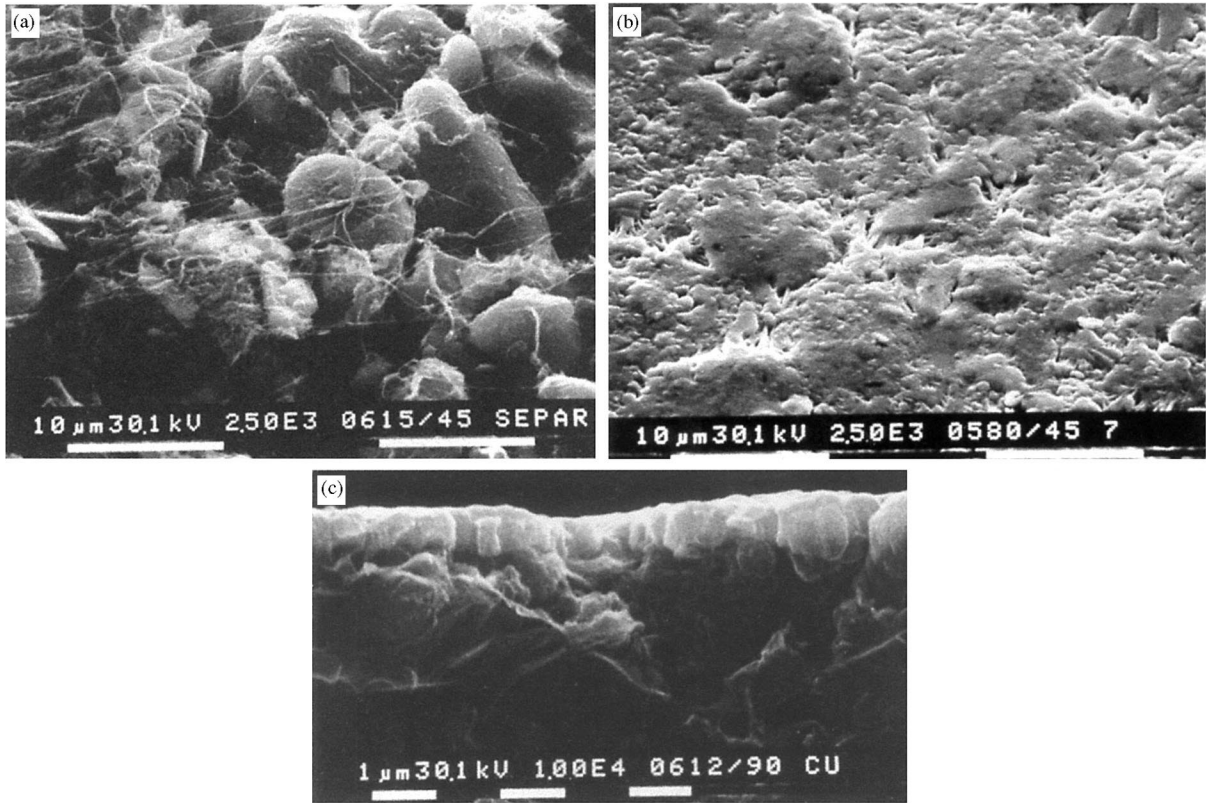


Fig. 2. SEM photos of the anode material showing (a) MCMB anode before rolling; (b) a top view of the copper deposited on the MCMB electrode; (c) cross-section of the copper-deposited electrode.

various weight fractions of UHMWPE. It can be seen that in the case of both the anode and the cathode materials both the strain and the stress at break increase with increasing polymer concentrations. The density of the cathode material

$\text{LiCoO}_2$  ( $\rho \approx 5.16 \text{ g/cm}^3$ ) was about a factor of two higher than the density of the anode MCMB ( $\rho = 2.25 \text{ g/cm}^3$ ). The density of polyethylene being close to unity, means that 1 wt.% polymer corresponds to 2.25 vol.% in MCMB and

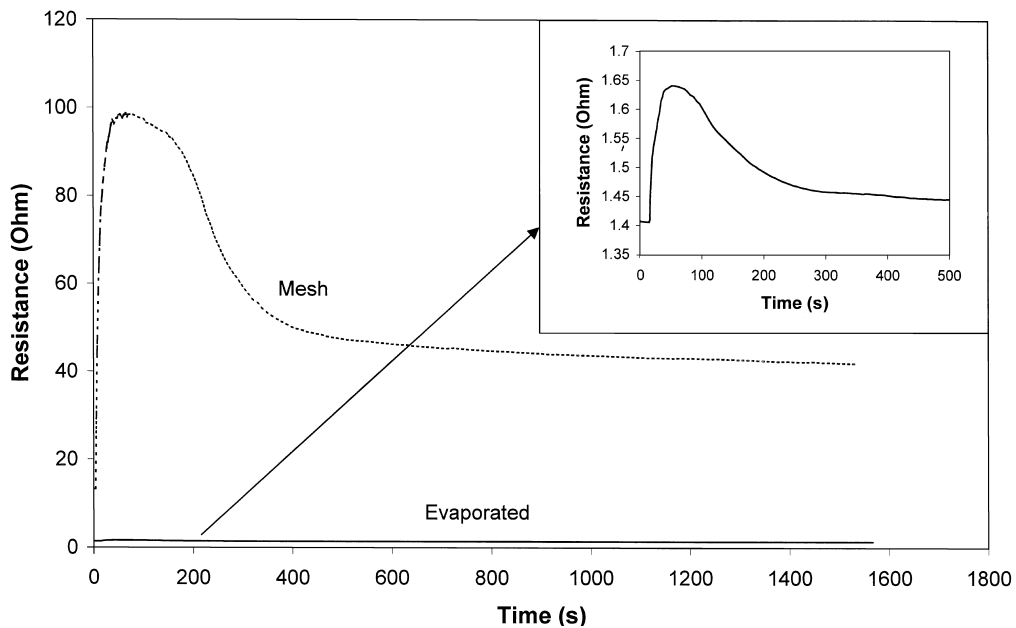


Fig. 3. Resistance as a function of time (---): 100 μm thick cathode sandwiched between 10 μm aluminium mesh; electrodes time (—): cathode material with evaporated electrodes.

5.16 vol.% in  $\text{LiCoO}_2$ . Furthermore particle size of the cathode material is about five times larger than that of the anode material. The fact that the anode and cathode materials have about the same strength at a given weight fraction of polymer indicates that the size of the particles probably also plays an important role in determining the strength of these materials.

In Fig. 1 it can be seen that free-standing electrodes produced using various amounts of UHMWPE can sustain considerable stress and strain without the need for the current collectors used in conventional lithium-ion and polymer batteries. Therefore instead of using the current collector as a carrier for the anode and cathode materials, we used free-standing films described above to support the current collectors which could be deposited on them as thin layers. This method has two main advantages: (i) it ensures good electrical contact between the electrodes and the

current collector; (ii) the amount of non-active material in the system is minimised, increasing the total capacity of the battery.

Current collectors of various thickness were deposited on the electrodes with a thickness of  $50\ \mu\text{m}$  by means of physical vapour deposition. The conductivity of the films on the anode and cathode materials depended on the surface quality of the electrodes. Using high-quality films with electrical conductivity values approaching that of the bulk could be obtained. The deposited layers were studied using SEM. Fig. 2(a) shows the MCMB anode material and polymeric binder holding the particles together before the rolling. A top view of the copper deposited on one side of the anode material is shown in Fig. 2(b). The porous structure which can be seen here is a template of the underground structure. Here it is important to point out that this porous structure is very significant because it facilitates fast absorp-

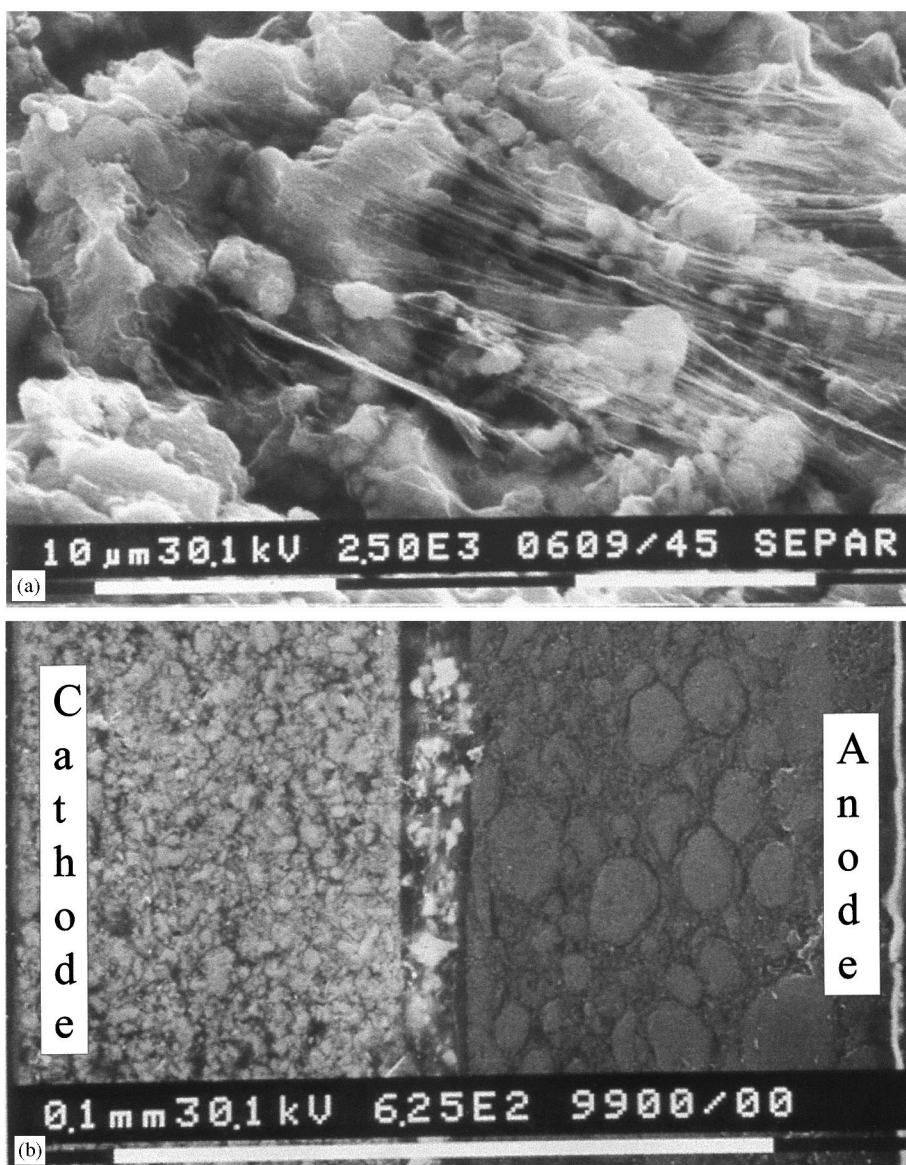


Fig. 4. (a) SEM photos of the separator; (b) cross-section of the laminated cell.

tion of liquid electrolyte by the cell during its activation, as will be described below. The cross-section of the copper deposited anode material is shown in Fig. 2(c). A 1  $\mu\text{m}$  thick copper layer which is in good contact with its underground is visible. The quality of the electrical contact between the electrodes and the evaporated current collector was compared with that between the layers of electrodes and a metal mesh current collector introduced inside it. For this purpose, 1  $\mu\text{m}$  thick layer of aluminium with an area of 1.76  $\text{cm}^2$  was evaporated onto each side of a 100  $\mu\text{m}$  thick cathode material. In the second case two 10  $\mu\text{m}$  thick aluminium mesh current collectors with the same area as above were alternately placed between three cathode materials and pressed together under heat. The thickness of the cathode material between the mesh current collectors was 100  $\mu\text{m}$ . The resistance between the current collectors was measured for the two systems as a function of time during wetting in acetone and subsequent drying in air. Acetone was used to simulate the volume changes, which occur during the activation of the cell in the electrolyte and volume changes induced during charge/discharge cycles. The results are shown in Fig. 3. It can be seen that in the case of the evaporated electrodes the initial low resistance increased slightly during the soaking of the electrode, to return to its initial value after the acetone had evaporated out of the system. This initial slight increase in resistance is associated mainly with decreased contact between the particles of the cathode material due to the expansion caused by the acetone. In the case of the system containing mesh electrodes, wetting it with acetone caused a very large increase in the resistance, which did not recover after the samples had dried. This behaviour is associated with decreased

electrical contact between the current collector and the electrodes because of swelling. This demonstrates the superior behaviour of the evaporated current collectors in having better electrical contact with the electrodes and maintaining it. The metal mesh electrodes that are often used in polymer batteries have contact problems and special care has to be taken to ensure good electrical contact and maintain it during the lifetime of the battery.

Porous separators were obtained by drawing films containing inert particles such as  $\text{LiLa}_{0.35}\text{Ti}_{0.55}\text{O}_3$  in 10 wt.% UHMWPE to about three times their original length. An electron micrograph of such a virgin separator is shown in Fig. 4(a). The porous structure which can absorb a large quantity of liquid is again clear. Separators were then placed between the anode and cathode materials and laminated under heat pressure to produce the cell cross-section is shown in Fig. 4(b). This lamination step can be done with or without a small amount of solvent (decaline). In the case of the dry samples the system had to be heated to above 160°C in order to obtain sufficient adhesion between the layers. On the other hand, when the separator was subjected to a small amount of decaline, sufficient adhesion between the layers was obtained already at 130°C. The second method is more attractive because it does not decrease the separator porosity, so samples with higher conductivity can be obtained. The effect of these treatments on the virgin separator is shown in Fig. 5, where the conductivity of 1 mol  $\text{LiPF}_6$  EC:DEC (1:1) electrolyte in the separators is plotted as a function of inverse temperature. It can be seen that the conductivity of the virgin separator obtained after drawing is the highest. Here it is important to note that  $\text{LiLa}_{0.35}\text{Ti}_{0.55}\text{O}_3$  which is known as solid state ion conductor does not

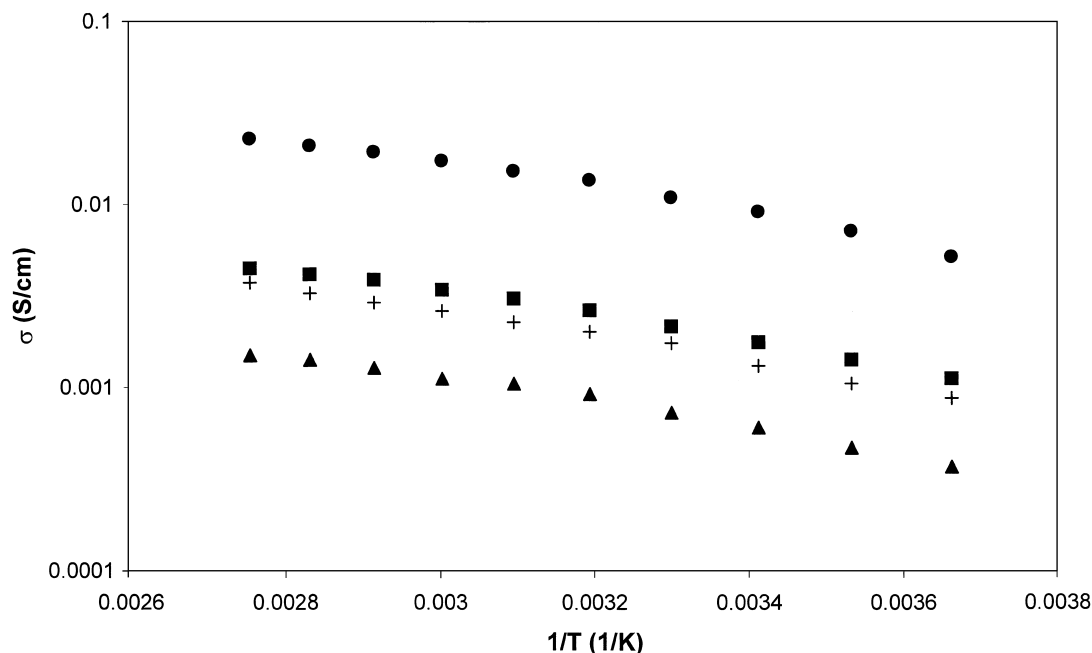


Fig. 5. Conductivity as a function of inverse temperature for 1 mol  $\text{LiPF}_6$  in EC:DEC (1:1). (●) pure electrolyte; (■) in virgin separator; (+) in separator after a heat treatment at 130°C in decaline; (▲) in separator after a heat treatment at 160°C.

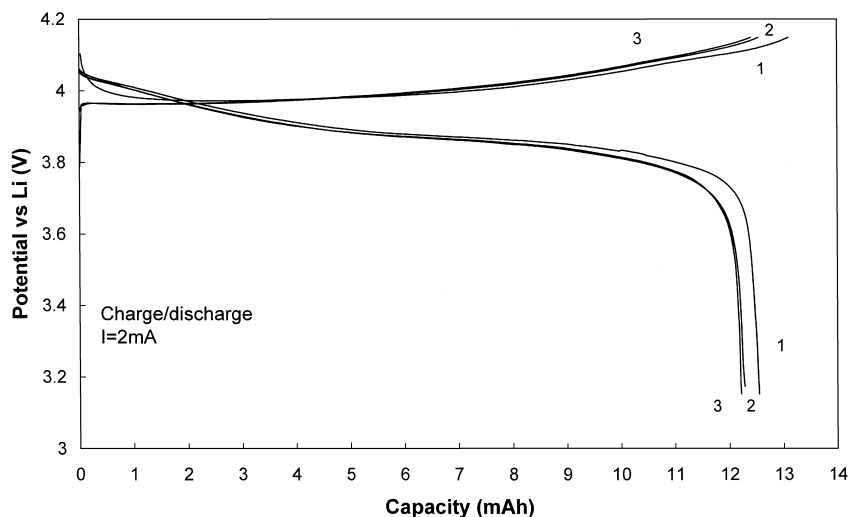


Fig. 6. Galvanostatic charge–discharge curves for LiCoO<sub>2</sub> electrode versus lithium at various cycles.

contribute to the conductivity of the system. The particles only help to create the porous structure. Therefore other particles such as Al<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub> can also be used for this purpose. The conductivity of the virgin separator, which was subjected to 160°C, is much lower. This is due to the decrease in the porosity of the separator. Subjecting the virgin separator to 130°C in the presence of decaline lead only a slight decrease in the porosity and therefore the conductivity of the electrolyte remained almost the same as in the virgin separator. Here it is also important to consider the conductivity of the samples at low temperatures. It can be seen that the conductivity of the samples in the separator as a function of temperature shows the same trend as in the bulk. This is due to the inert nature of the polymer which does not have an influence on the

conductivity behaviour of the electrolyte as a function of temperature.

### 3.1. Battery performance

Before describing the performance of the batteries produced using the free-standing anode and cathode materials described above, the cycling behaviour of the anode and cathode materials will be described separately. For this purpose, cells were produced by placing a commercial separator between metallic lithium and the electrode material and holding them together under pressure from outside. In galvanostatic experiments, a charge/discharge current of 2 mA was used. For the cathode material the voltage was limited to a maximum of 4.15 V during charging and to a

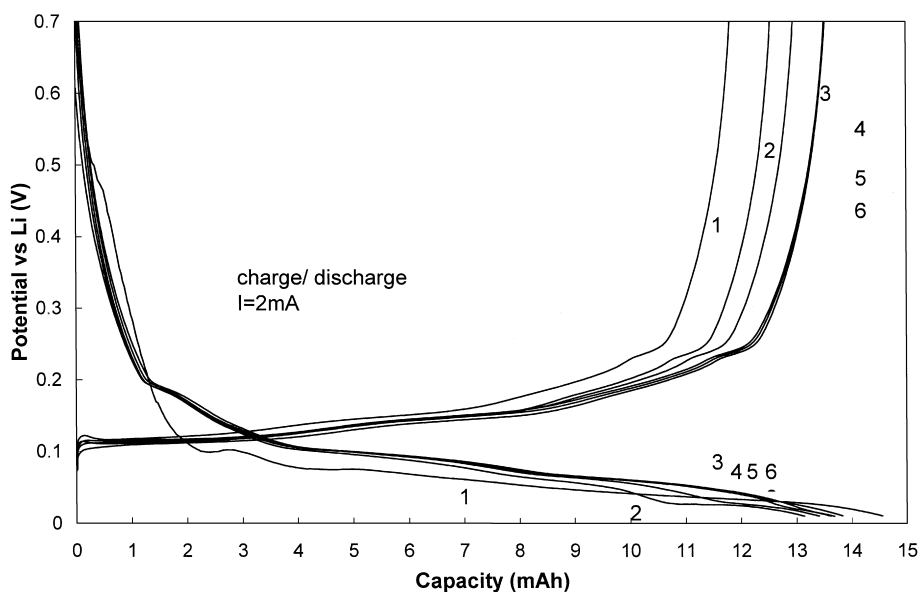


Fig. 7. Galvanostatic charge–discharge curves obtained for an MCMB electrode versus lithium at various cycles.

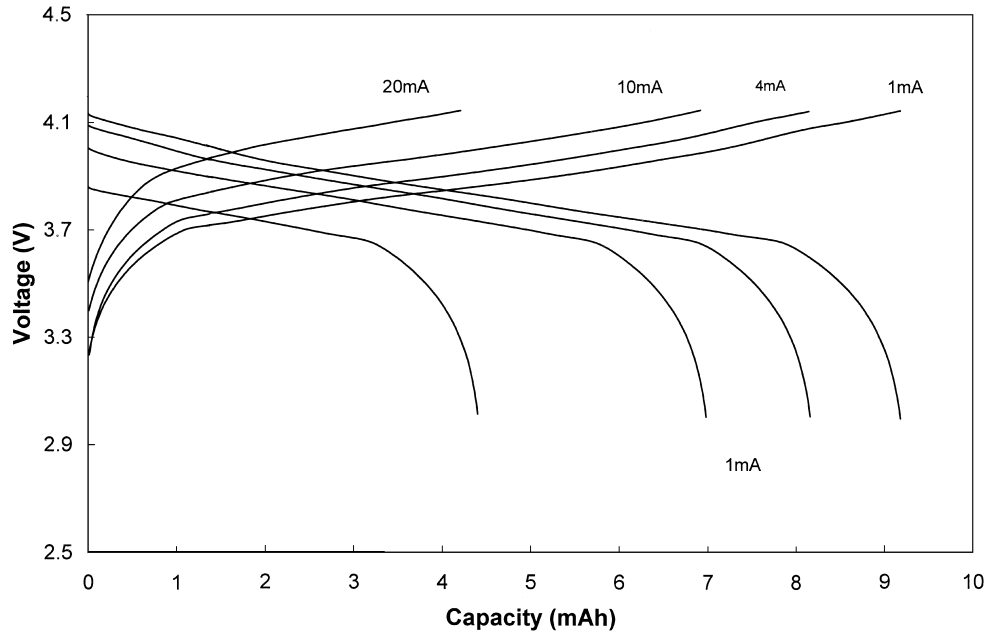


Fig. 8. High-rate charge capability of the battery. Charge curves obtained at various currents after discharging at 1 mA.

minimum of 3.0 V during discharge. The behaviour observed during the successive cycles is shown in Fig. 6. It can be seen that after a slight loss of capacity in the first cycle, the subsequent cycles showed almost 100% cycling efficiency for the cathode material. The behaviour of the MCMB electrode was tested in the same configuration. In this case the voltage was limited to a maximum of 1.4 V during charging and a minimum of 10 mV was used during discharge. The results are shown in Fig. 7. The behaviour observed here is typical of graphites. During the first few so-

called formation cycles irreversible reactions occurred on the electrode. These irreversible reactions are associated with electrolyte decomposition and lead to the formation of a passivating film or solid electrolyte interface.

Having investigated the electrodes separately, cells were produced by sandwiching a separator containing a small amount of decaline between the anode and cathode materials and subsequently heating the stack to 130°C. The performance of the cell was evaluated in galvanostatic experiments. In order to study the effect of the charge current, the

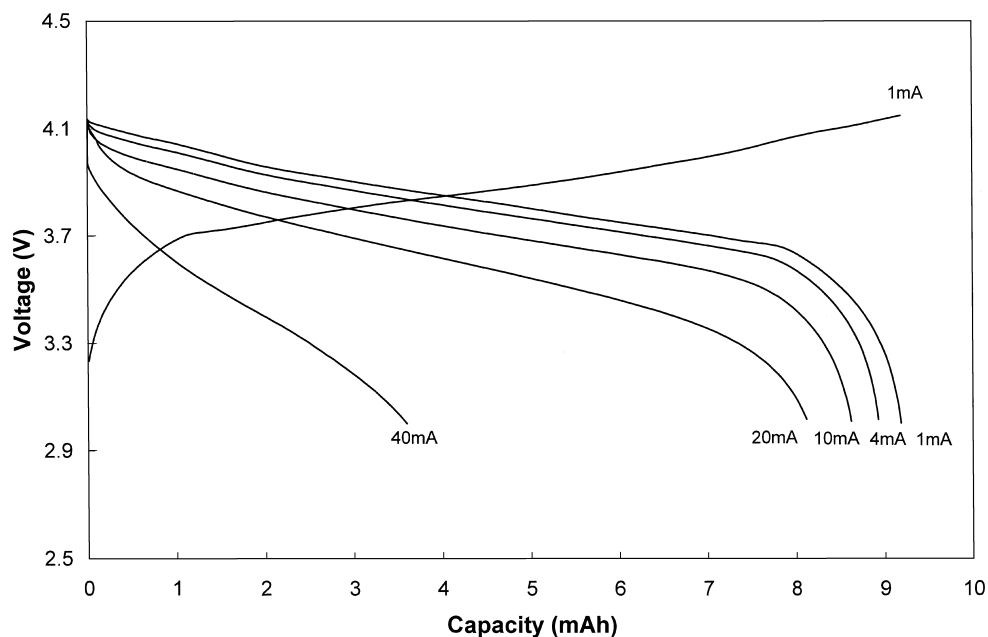


Fig. 9. High-rate discharge capability of the battery. Discharge curves obtained at various currents after charging at 1 mA.

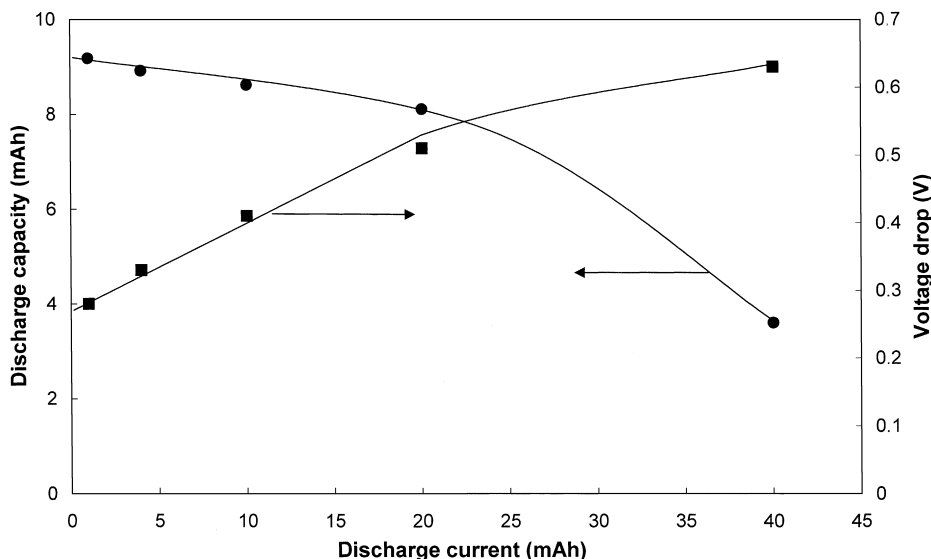


Fig. 10. Discharge capacity and voltage drop as functions of discharge current.

battery was charged using various currents and discharged at 1 mA. In all the experiments the voltage was limited to a maximum of 4.15 V during charging and to a minimum of 3.0 V was used during discharge. The result is shown in Fig. 8. It can be seen that the battery reached the set limit faster with increasing charge current density, so the charge capacity decrease. When the battery was discharged at 1 mA, the charge was totally recovered. In a similar experiment, the battery was charged at a current of 1 mA and then discharged at various rates. The results of this experiment are shown in Fig. 9. It can again be seen that the discharge capacity of the battery is lower at high discharge rates. In both figures the observed effect is typical of Li-ion batteries. It reflects the effect of battery's internal resistance. The internal resistance is roughly related to the voltage drop ( $V_d$ ),

which is the difference between the battery's actual voltage ( $V_{mea}$ ) and its open-circuit voltage ( $V_{oc}$ ). In Fig. 10 both the discharge capacity and the voltage drop at half discharge capacity have been plotted as a function of the discharge current. It can be seen that up to the discharge current of 20 mA both the discharge capacity and the voltage drop are almost linear functions of the discharge current. Using the slope of the linear part of the curve the average internal resistance was estimated to be about  $10 \Omega$  for a battery with a surface area of  $5.3 \text{ cm}^2$ .

The high rate cycling behaviour of the battery was investigated by measuring the discharge capacity of the battery using a 4 mA charge/discharge current in galvanostatic experiments. The full capacity of the battery was regularly checked using a 1 mA charge/discharge current.

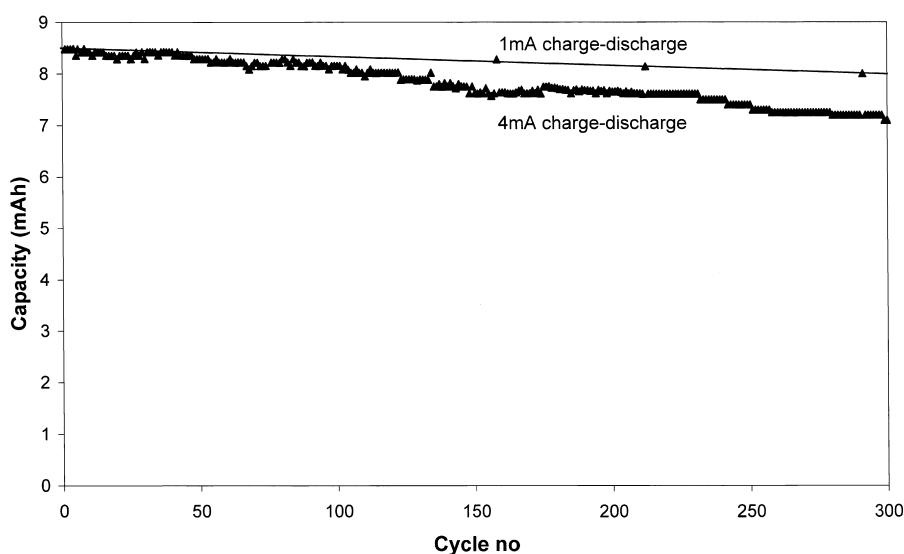


Fig. 11. Discharge capacity as a function of cycle number.



The results are shown in Fig. 11. It can be seen that at 4 mA the capacity of the battery decreases whereas at 1 mA the capacity shows only a slight change. These results show that the intrinsic capacity of the battery changes only slightly in 300 cycles. The cause of the apparent decrease at 4 mA is caused by the increase in the battery's internal resistance. However, it is not clear whether this is caused by the separator or the electrode structure.

#### 4. Conclusions

A new polymer battery concept has been demonstrated. One weight percent UHMW polyethylene proved to be sufficient to produce free-standing anode and cathode materials. These films were coated with thin layers of current collectors by means of physical vapour deposition. The current collectors were porous and had very good electrical contact with the underground. Separators were

produced using the same polymer and inert particles of  $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ . The components were laminated under heat and pressure and a single flat cell was produced. During the activation of the cell the electrolyte was very quickly absorbed from all sides thanks to the cell's highly porous structure. The battery was sealed in a laminated bag for protection. It could be charged and discharged at very high rates. After 300 cycles times only a slight decrease in the capacity of the battery was observed.

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